Solvent-Dependent Quenching of the Lowest Excited Singlet State of 9,10-Dichloroanthracene by Ground-State 2,5-Dimethylhexa-2,4-diene Yielding 9-Chloroanthracene in Acetonitrile or the [4+2]Adduct in *n*-Heptane

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In acetonitrile, an exciplex formed between the lowest excited singlet state (^{1}DCA*) of 9,10-dichloroanthracene (DCA) and ground-state 2,5-dimethylhexa-2,4-diene (DMHD) generates the DCA radical anion as an intermediate for dechlorination of DCA yielding 9-chloroanthracene. In *n*-heptane, however, quenching of ^{1}DCA* by DMHD forms no exciplex and a dibenzobicyclo[2.2.2]octadiene-type compound (the [4+2] adduct) is obtained as the final product.

In acetonitrile (CH_3CN) containing *N,N*-dimethylaniline (DMA) or triethylamine (TEA), nanosecond laser photolysis and steady-state photolysis of 9,10-dichloroanthracene (DCA)[1] and 9,10-dibromoanthracene (DBA)[2] reveal that the intermediates for their dehalogenation yielding 9-haloanthracenes are the haloanthracene radical anions. Furthermore, picosecond laser photolysis of DBA in CH_3CN-DMA reveals that formation of an exciplex between the lowest excited singlet state (^{1}DBA*) of DBA and ground-state DMA is followed by decomposition into the DBA radical anion ($DBA^{\bullet -}$) and the DMA radical cation.[3] In CH_3CN-TEA, however, no exciplex formation can be seen but nanosecond laser photolysis reveals the existence of $DBA^{\bullet -}$. It thus is proposed that quenching of ^{1}DBA* by TEA in CH_3CN forms a non-emissive short-lived encounter complex or ion pair followed by rapid generation of $DBA^{\bullet -}$. The present paper deals with the excited-state dynamics of DCA in CH_3CN and *n*-heptane (HP) containing 2,5-dimethylhexa-2,4-diene (DMHD), because the final photoproduct in CH_3CN is 9-chloroanthracene (CA) but that in HP is a dibenzobicyclo[2.2.2]octadiene-type compound (the [4+2] adduct).

DCA (Aldrich) was recrystallized three times from ethanol. DMHD (Aldrich) was distilled immediately before use and spectral-grade CH_3CN (Dojin) was dried using molecular sieves 3A (Wako); spectral-grade HP (Dojin) was used without further purification. The sample solution was not degassed and sub-picosecond laser photolysis at room temperature was performed using the second harmonic (400 nm) from a femtosecond mode-locked Ti:sapphire laser amplified by a regenerative amplifier.[4]

As shown in Figure 1a, the transient absorption spectra obtained in CH_3CN-DMHD(1 M) indicate that an absorption (band B_M with λ_{max}=595 nm) decreases with time accompanied by the increment and then decrement of another absorption (band B_E with λ_{max} =680 nm). Bands B_M and B_E are assigned to absorptions of the lowest excited singlet state (^{1}DCA*) of DCA and an exciplex [^{1}(DCA-DMHD)*] of ^{1}DCA* with DMHD, respectively. This is based on the following facts; (1) band B_M is very similar to the singlet-singlet ($S' \leftarrow S_1$) absorption band due to ^{1}DBA*;[3] (2) in the absence of DMHD, the decay rate constant of $S' \leftarrow S_1$ absorption due to ^{1}DCA* is equal to its fluorescence decay rate constant (k_M=1.2x10^8 s^{-1});[1] (3) band B_E is similar to the absorption band due to an exciplex of ^{1}DBA* with amine (DMA or TEA);[3] (4) addition of DMHD (0.5 or 1 M) in CH_3CN gives rise to the appearance of a broad emission band ($\lambda_{max} \approx$540 nm) similar to those of ^{1}DBA*-amine exciplexes.[3]

As shown in Figure 2, the absorbance changes of bands B_M [$A_M(t)/A_M(max)$] and B_E [$A_E(t)/A_E(max)$] with time suggest that the band intensities reach the constant values at delay times longer than 1

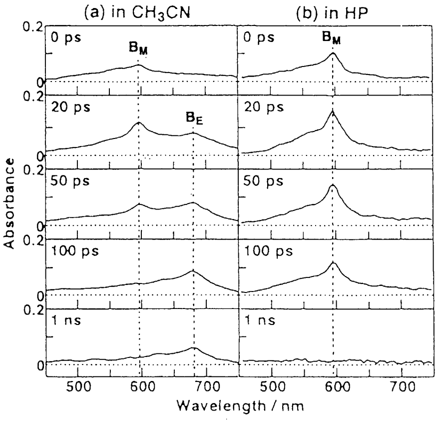

Figure 1. Transient absorption spectra obtained by sub-picosecond laser photolysis of DCA in (a) CH_3CN and (b) HP containing 1 M DMHD.

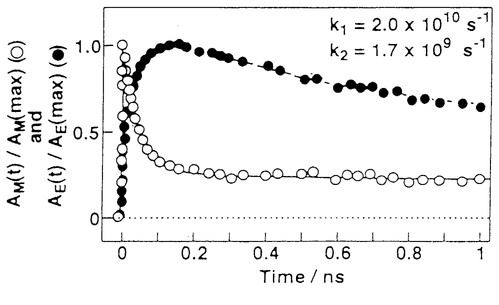

Figure 2. $A_M(t)/A_M(max)$ [monitored at 595 nm (○)] and $A_E(t)/A_E(max)$ [monitored at 680 nm (●)] obtained in CH_3CN-DMHD(1 M). The solid and dashed biexponential functions (with rate constants k_1 and k_2) are the best-fit absorbances calculated for the superposition of absorptions due to ^{1}DCA*, ^{1}(DCA-DMHD)* and $DCA^{\bullet -}$.

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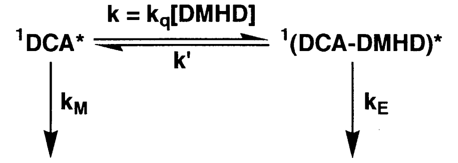
ns. The residual absorption band observed after the disappearance of ^{1}(DCA-DMHD)* can be ascribed to the absorption of the DCA radical anion ($DCA^{\bullet -}$), because the spectrum at 1 ns delay shown in Figure 1a is similar to that of $DCA^{\bullet -}$ obtained by nanosecond laser photolysis of DCA in CH_3CN containing 1 M DMHD[5] or amine (DMA or TEA).[1] The solid and dashed bi-exponential functions (with rate constants k_1 and k_2) shown in Figure 2 are the best-fit absorbances calculated as follows; (1) both bands B_M and B_E are interpreted in terms of the superposition of absorptions due to ^{1}DCA*, ^{1}(DCA-DMHD)* and $DCA^{\bullet -}$, and their concentrations at a given delay time are calculated on the basis of Scheme 1;[6] (2) a Gaussian intensity function with a full width at the half-maximum intensity of 0.25 ps is assumed for both the excitation and probing light pulses. Hence, the sum of rate constants k_1 and k_2 should be equal to $k_q[DMHD]+k'+k_E+k_M$.[6] If ^{1}(DCA-DMHD)* is formed by diffusion-controlled quenching of ^{1}DCA* by DMHD, the corresponding rate constant ($k_q=1.9\times10^{10}$ M^{-1} s^{-1}) can be estimated by the Debye-Smoluchowski equation ($k_q=8RT/3000\,\eta$) using the viscosity ($\eta=0.345$ cp) of CH_3CN at 25 ^oC. And then, $k'+k_E=2.6\times10^9$ s^{-1} is obtained by a choice of [DMHD]=1 M, $k_1=2.0\times10^{10}$ s^{-1} and $k_2=1.7\times10^9$ s^{-1}. On the basis of Scheme 1, the efficiency for repopulation of ^{1}DCA* from ^{1}(DCA-DMHD)* can be defined by $\gamma=k'/(k'+k_E)$ and $k_q(1-\gamma)/k_M$ should be equal to 69.1 M^{-1} which is the slope of straight line obtained by a Stern-Volmer plot of the ^{1}DCA* fluorescence intensity against the concentration of DMHD. Since $\gamma=k'/(k'+k_E)$ is found to be 0.58, a combination of this value with $k'+k_E=2.6\times10^9$ s^{-1} indicates that the decay rate constants of ^{1}(DCA-DMHD)* are $k'=1.5\times10^9$ s^{-1} and $k_E=1.1\times10^9$ s^{-1} which are comparable with those ($k'=2.7\times10^9$ s^{-1} and $k_E=4.8\times10^9$ s^{-1}) obtained for the ^{1}DBA*-DMA exciplex in CH_3CN.[3]



Scheme 1.

We thus believe that $DCA^{\bullet -}$ generated by decomposition of ^{1}(DCA-DMHD)* is an intermediate for dechlorination of DCA yielding CA. Meanwhile, Smothers et al.[7] have reported that ^{1}(DCA-DMHD)* is formed not only by a reaction of ^{1}DCA* with DMHD but also by direct excitation of a ground-state DCA-DMHD complex. If this is correct, one should observe the buildup of absorption due to ^{1}(DCA-DMHD)* within a duration of the excitation light pulse. In contrast, Figure 2 indicates that band B_E never grows in within a duration of sub-picosecond pulse excitation. Furthermore, examination of the absorption spectral change of DCA upon addition of DMHD in CH_3CN reflects no formation of the ground-state DCA-DMHD complex. Although formation of a triplex betweween ^{1}(DCA-DMHD)* and DMHD is also reported by Smothers et al.,[7] no such an evidence has been obtained, i.e., the results obtained in CH_3CN-DMHD can well be explained by Scheme 1.

Upon steady-state photolysis of DCA in HP-DMHD(1 M), we have observed formation of a dibenzobicyclo-[2.2.2]octadiene-type compound (the [4+2] adduct). Although Saltiel et al.[8] have reported that ^{1}(DCA-DMHD)* is the precursor for formation of this [4+2] adduct in benzene-DMHD, no emission and absorption due to ^{1}(DCA-DMHD)* can be seen not only in benzene-DMHD but also in HP-DMHD, i.e., normalization of the $S' \leftarrow S_1$ absorption spectrum (obtained in HP without DMHD) to all the transient absorption spectra shown in Figure 1b reveals no existence of an absorption band due to ^{1}(DCA-DMHD)*. In HP-DMHD(1 M), furthermore, an intensity plot of band B_M against time indicates that ^{1}DCA* is populated within a duration of sub-picosecond pulse excitation and then disappears following a single-exponential function with a decay rate constant of $k_D=6.0\times10^9$ s^{-1}. Hence, a choice of the decay rate constant ($k_M=1.2\times10^8$ s^{-1}) obtained for ^{1}DCA* in HP without DMHD gives the quenching rate constant of ^{1}DCA* by 1 M DMHD to be $k_q=(k_D-k_M)/[DMHD]=5.9\times10^9$ M^{-1} s^{-1}. Dividing k_q thus obtained by k_M, one can get the value of 49.2 M^{-1} which is nearly equal to the slope (51.7 M^{-1}) of straight line obtained by a Stern-Volmer plot of the ^{1}DCA* fluorescence intensity against the concentration of DMHD in HP. This indicates that quenching of ^{1}DCA* by DMHD is a diffusion-controlled reaction. Since [4+2] addition of DMHD to ^{1}DCA* is forbidden,[9] we suppose that quenching of ^{1}DCA* by DMHD in HP causes stepwise reactions yielding the [4+2] adduct finally. Experimental works along this line are in progress.

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